Self-consistent *GW* Method

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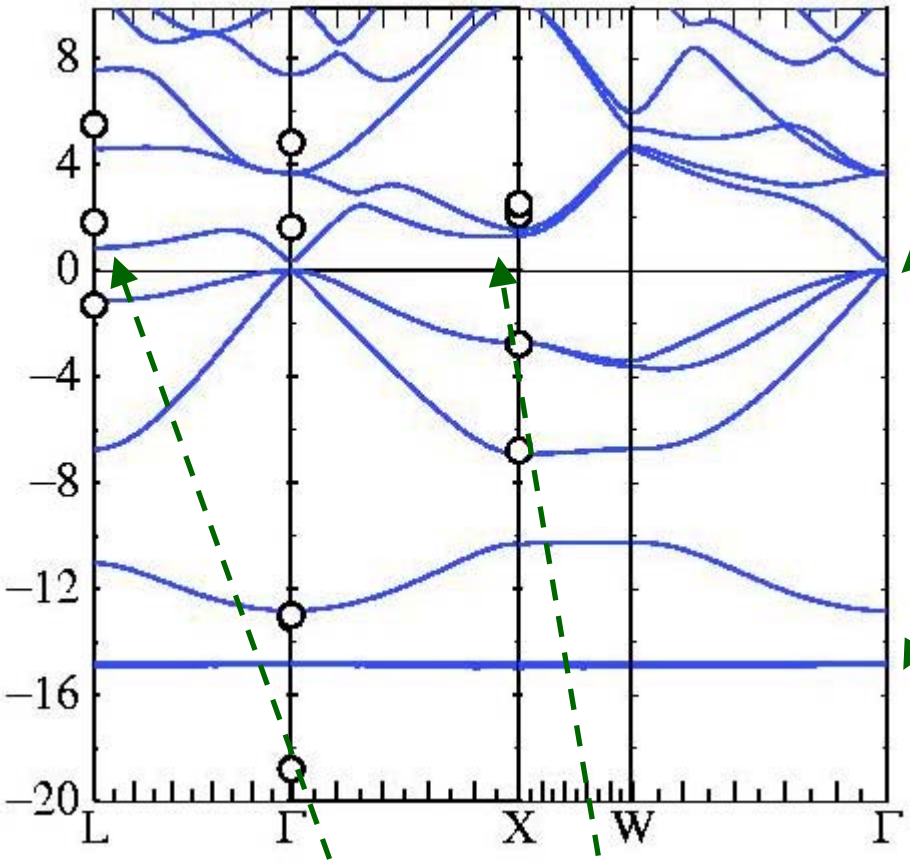
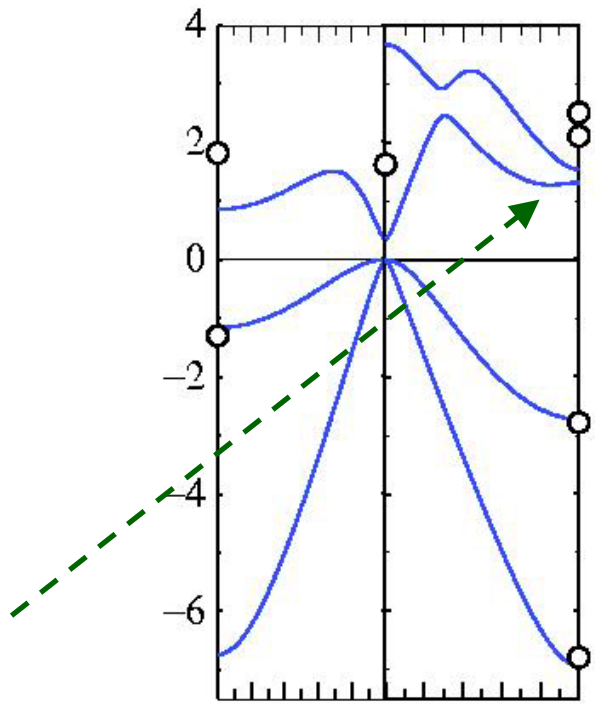
- **A new kind self-consistent *GW* (scGW) approximation**
  - **Self-consistency in charge density *n***
  - **Not related to the LDA**
  - **Stay within Landau QP picture — sharp QP spectra**
    - **"Best possible" mean-field approximation — excellent starting point for DMFT calculations**
- **Apply to:**
  - **NiO, MnO**
  - **Many ZB semiconductors, ZB and others**
  - **Ni,Cu**
- **Total energies? (Miyake)**



Consider LDA bands of bulk GaAs.

- Fundamental gap too small
  (expt+SO=1.63 eV)
  (LDA =0.32 eV)
- Ga *d* level too shallow
  (expt = -18.8 eV)
  (LDA = -15.0 eV)



- $\Gamma_{1c} \rightarrow L_{1c}$, $\Gamma_{1c} \rightarrow X_{1c}$ transitions too large
  (expt = 0.48 eV; LDA = 0.97 eV)
- Effective mass 3× too small
  (expt = 0.067 m_0; LDA= 0.022 m_0)

Local minimum along (Γ→X) not at X!

GW approximation (Hedin, 1965)

GW Self-energy is

$$\Sigma(r,r',\omega) = \frac{i}{2\pi}\int d\omega' G(r,r',\omega+\omega') e^{i\delta\omega'} W(r'',r',\omega')$$

where

G is the one-particle Green's function

W is the screened Coulomb interaction

$$W(r,r',\omega) = \int dr'' \varepsilon^{-1}(r,r'',\omega) V(r'',r')$$

ε = RPA dielectric function = $(1-vD)$ where D = polarization function

Usual *GW* is non self-consistent: $G \rightarrow G_0$, computed from LDA

$$\left(\omega + \frac{\nabla^2}{2m} - v_{\text{ext}} - v_H - v_{xc}^{\text{LDA}}\right) G_0 = \delta(\mathbf{r}-\mathbf{r}')$$

Implementations of *GW* differ in the following:

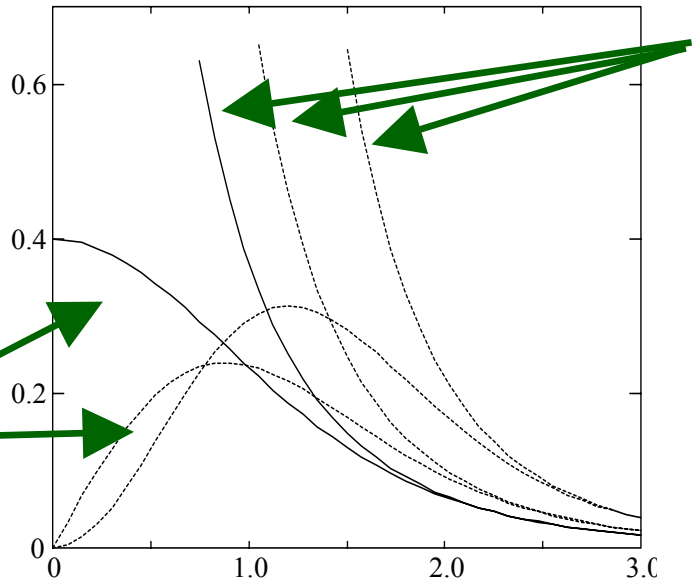
- Choice of basis for one-electron (usu. LDA) wave functions
- Choice of basis for screened Coulomb interaction *W*
- Treatment of core
- Use of plasmon-pole approximation
- Approximations to potential (e.g. PP; ASA; semilocal Σ)
- Self-consistency

Present work:

- LDA basis: smoothed Hankels + local orbitals
- *W* expanded in IPW + product basis inside MT spheres
- Core treated on footing similar to valence (HF at lowest level)
- No plasmon-pole approximation
- Full-potential treatment (features in common w/ LAPW, PAW)
- New kind of self-consistency

LMTO Basis for All-Electron *GW* method

§Eigenstates expanded as generalized Linear Muffin-Tin Orbitals (both efficient and accurate).



Smoothed Hankels: envelopes $\rightarrow r^{\,l}$ as $r \rightarrow 0$.

Standard LMTO basis: envelopes $\rightarrow r^{\,-l}$ as $r \rightarrow 0$

Solves S-eqn for flat $V = V_{MTZ}$.

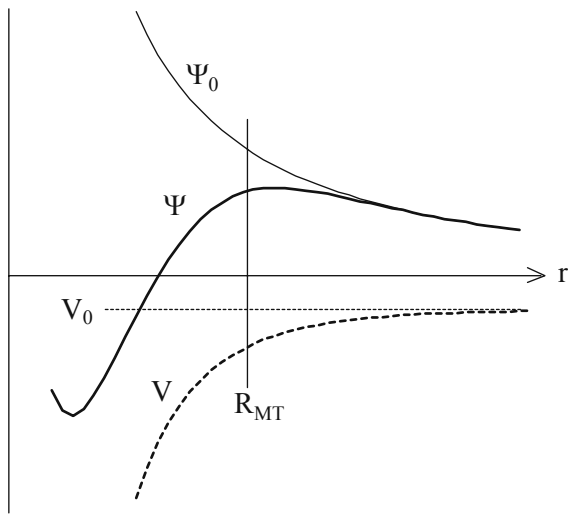
$$H_s(\varepsilon, r) = \frac{1}{r} e^{-\sqrt{-\varepsilon} r}$$

$$\left(\Delta + \varepsilon\right) H_L(r_s, \mathbf{r}) = -4\pi G_L(r_s, \mathbf{r}) = -4\pi Y_L(-\nabla) g_0(r_s, r)$$

$$H_L(\varepsilon, r_s, \mathbf{q}) = \frac{-4\pi}{\varepsilon - \mathbf{q}^2} e^{4(\varepsilon - q^2)/r_s^2} Y_L(-i\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}}$$

Solves Schrodinger eqn for this potential

$$V(\mathbf{r}) = V_{MTZ} - 4\pi G_L(r_s, \mathbf{r}) / H_L(r_s, \mathbf{r})$$



§ Local orbitals can be included to augment linear combinations of ϕ and $\dot{\phi}$ (linear method):

Extra orbitals $\phi_z = \phi(\varepsilon_z) - A\phi - B\dot{\phi}$ can be chosen with A,B s.t. $\phi_z(r_{MT})=0$ and $\phi_z'(r_{MT})=0$ (no interstitial part)

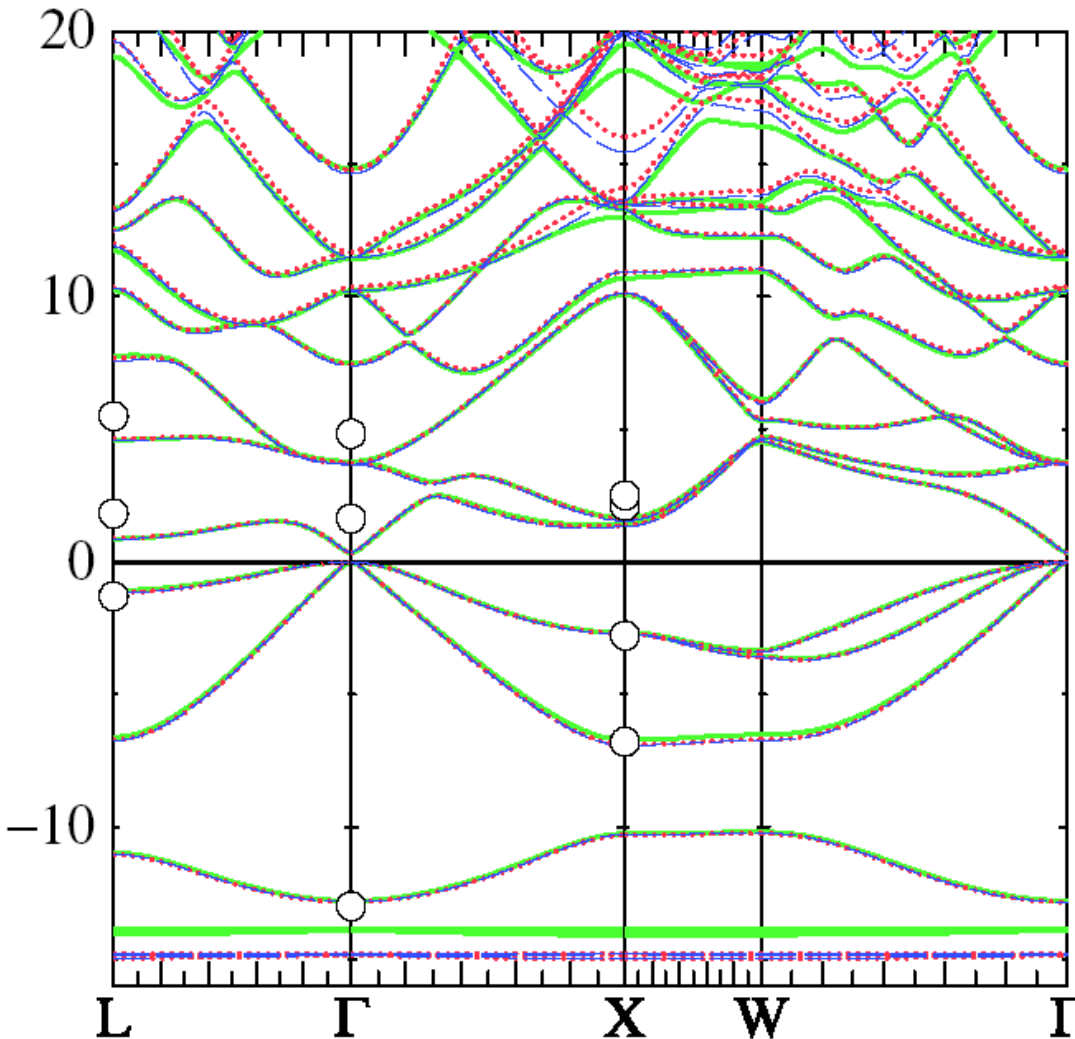
Energy bands accurate over a wide energy window.

Example : GaAs

Blue : this method (Methfessel and van S.)

Red: old FP-LMTO method (Methfessel and van S.)

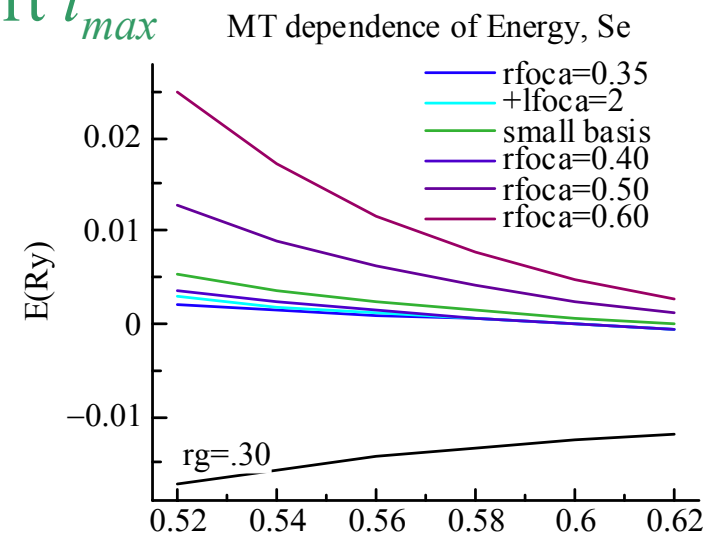
Green: QMTO-ASA (Andersen) — bands from 2nd gen. ASA $V(r)$.

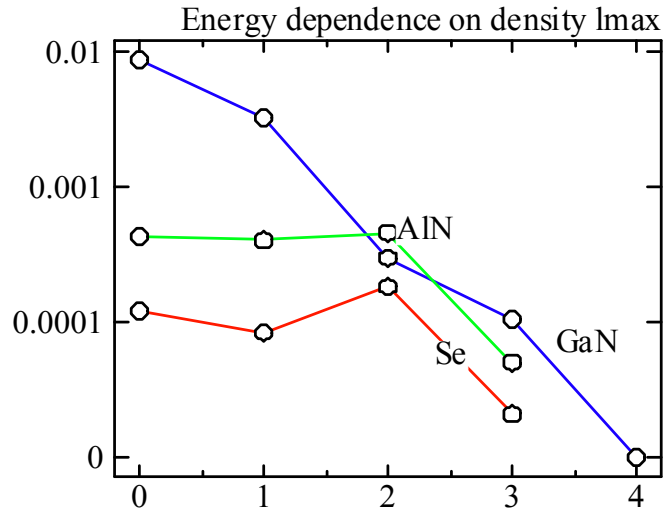


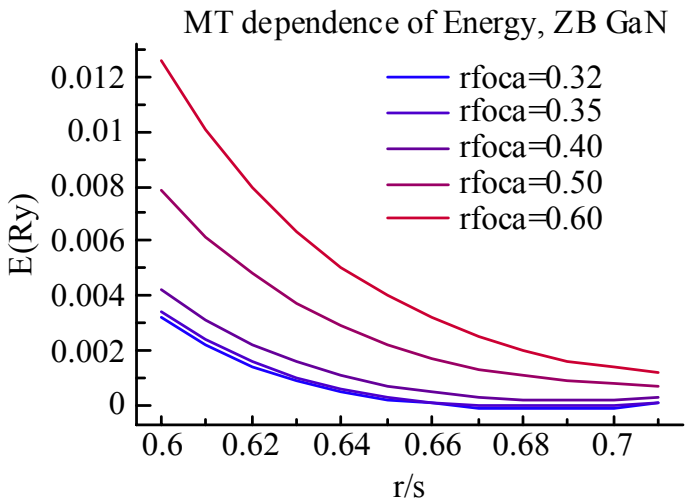
§Very weak dependence of E_{tot}(LDA), QP levels ε_n on r_{MT}

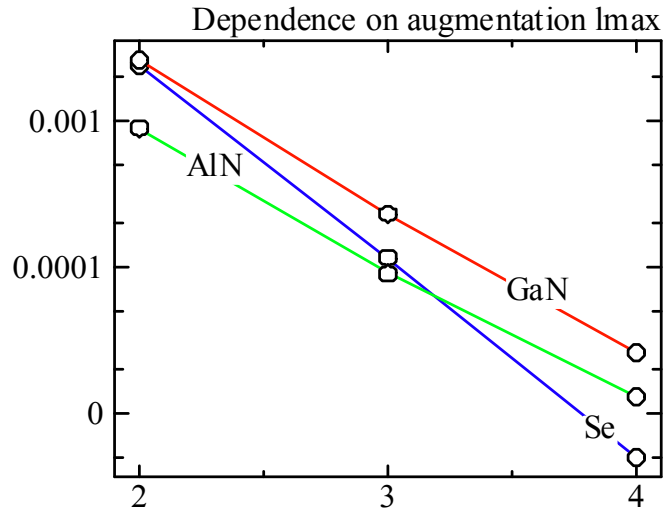
§Very rapid convergence wrt l_{max} (like PAW)

Future: Better envelope functions: screen; KE →continous at r_{MT} (NMTO).









Basis sets for *GW*

Two independent basis sets are required.

Orbital basis Φ for wave functions. Then

$$G(\mathbf{r}t,\mathbf{r}'t') = \int \frac{d\omega}{2\pi} \sum_{\mathbf{k}} e^{-i\omega(t-t')} \sum_{ij} G_{ij}(\mathbf{k},\omega)\Phi_i^{\mathbf{k}}(\mathbf{r})\,\Phi_j^{\mathbf{k}}(\mathbf{r}')$$

Both basis functions Φ_i and eigenstates $\psi_i^{\mathbf{k}n}$ are expanded:

in augmented waves ϕ inside MT spheres

in plane waves in the interstitial

$$G_{ij}(\mathbf{k},\omega) = \sum_n \frac{\psi_i^{\mathbf{k}n}\psi_j^{*\mathbf{k}n}}{\omega - \varepsilon_n^{\mathbf{k}} \mp i\delta}$$

$\psi_i^{\mathbf{k}n}$ and $\varepsilon_n{}^{\mathbf{k}}$ are found from solutions of the Schrodinger equation

$$\sum_j \left(-\frac{\nabla^2}{2m} + v_{\text{ext}} + V_{\text{H}ij}^{\mathbf{k}} + \Sigma_{ij}(\mathbf{k},\omega) \right) \psi_j^{\mathbf{k}n} = \varepsilon_n^{\mathbf{k}} \psi_i^{\mathbf{k}n}$$

Basis sets for *GW*, continued

§Basis for eigenfunctions (Consider 1st iteration only)

Eigenfunctions $\psi^{\mathbf{k}n}$ expanded in MTO's χ_s ← Labels site, *l*, other attributes

$$\psi^{\mathbf{k}n}(\mathbf{r}) = \sum_s u_s^{\mathbf{k}n} \chi_s(\mathbf{r})$$

Local orbital

For augmented-waves MTO's χ_s are expanded by:

- local functions ϕ_{RLi} inside MT spheres, i=1..2 or 1..3
- IPW in the interstitial:

$$P_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) = \begin{cases} 0 & \text{if } \mathbf{r} \in \text{ any MT sphere} \\ \exp\left[i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}\right] & \text{otherwise} \end{cases}$$

Then

$$\psi^{\mathbf{k}n}(\mathbf{r}) = \sum_{ai} \alpha_{ai}^{\mathbf{k}n} \phi_{ai}^{\mathbf{k}}(\mathbf{r}) + \sum_{\mathbf{G}} \beta_{\mathbf{G}}^{\mathbf{k}n} P_{\mathbf{G}}^{\mathbf{k}n}(\mathbf{r})$$

Note: formalism applies equally to LAPW

Basis sets for *GW*, continued

§For v, W we need $\langle\psi\psi|v|\psi\psi\rangle = \langle\psi\psi|M\rangle\langle M|v|M\rangle\langle M|\psi\psi\rangle$

M = intermediate basis for expansion of products $\psi\psi$.

M: product basis B=$\{\phi\times\phi\}$ inside MT spheres (Aryasetiawan)

Plane waves $P\times P\rightarrow P$ in the interstitial (conventional methods)

Therefore:

A complete basis M for products $\psi\psi$ is: $M \equiv \left\{P_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}), B_I^{\mathbf{k}}(\mathbf{r})\right\}$

Now

$$\psi^{\mathbf{k}n}(\mathbf{r}) = \sum_{ai} \alpha_{ai}^{\mathbf{k}n}\phi_{ai}^{\mathbf{k}}(\mathbf{r}) + \sum_{\mathbf{G}} \beta_{\mathbf{G}}^{\mathbf{k}n} P_{\mathbf{G}}^{\mathbf{k}n}(\mathbf{r})$$

$$\psi^{\mathbf{k}_1 n_1}(\mathbf{r})\psi^{\mathbf{k}_2 n_2}(\mathbf{r}) = \sum_{ai} B_{RI}^{\mathbf{k}_1+\mathbf{k}_2}(\mathbf{r}) \times \langle B|\phi\phi\rangle \times \alpha \times \alpha$$

$$+ \sum_{\mathbf{G}} P_{\mathbf{G}}^{\mathbf{k}_1+\mathbf{k}_2}(\mathbf{r}) \times \langle P|PP\rangle \times \beta \times \beta$$

For a given potential and basis, make these quantities:

Eigenfunctions $\psi_{\mathbf{k}n}$ and eigenvalues $\varepsilon_{\mathbf{k}n}$

Coulomb matrix $$v_{IJ}(\mathbf{k}) = \left\langle M_I^{\mathbf{k}} \middle| v \middle| M_J^{\mathbf{k}} \right\rangle, I = \{RLi, \mathbf{G}\}$$

Eigenfunction products $$\left\langle \psi_{\mathbf{q}j} \middle| \psi_{\mathbf{q}-\mathbf{k}i} M_I^{\mathbf{k}} \right\rangle, I = \{RLi, \mathbf{G}\}$$

Now we can carry out *GW* cycle. Make : Σ_X, D, W, Σ_C:

Exchange part Σ_X of self-energy

$$\left\langle \mathbf{q}j \middle| \Sigma_X \middle| \mathbf{q}j \right\rangle = \sum_{\mathbf{k}}^{BZ} \sum_{i}^{occ} \left\langle \psi_{\mathbf{q}j} \middle| \psi_{\mathbf{q}-\mathbf{k}i} \tilde{M}_I^{\mathbf{k}} \right\rangle v_{IJ}(\mathbf{k}) \left\langle \tilde{M}_J^{\mathbf{k}} \psi_{\mathbf{q}-\mathbf{k}i} \middle| \psi_{\mathbf{q}j} \right\rangle$$

Where the M must be orthogonalized

$$v(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{k},I,J}^{BZ} \left| \tilde{M}_I^{\mathbf{k}} \right\rangle v_{IJ}(\mathbf{k}) \left\langle \tilde{M}_J^{\mathbf{k}} \right| \qquad \left| \tilde{M}_I^{\mathbf{k}} \right\rangle = \sum_J \left| M_J^{\mathbf{k}} \right\rangle \left\langle M_J^{\mathbf{k}} \middle| M_I^{\mathbf{k}} \right\rangle^{-1}$$

Polarization function D

$$= \sum_{\mathbf{k}}^{\mathrm{BZ}} \sum_{j}^{\mathrm{occ}} \sum_{i}^{\mathrm{unocc}} \langle M_I^{\mathbf{k}} \Psi_{\mathbf{q}j} | \Psi_{\mathbf{q}-\mathbf{k}i} \rangle \langle \Psi_{\mathbf{q}j} | \Psi_{\mathbf{q}-\mathbf{k}i} M_J^{\mathbf{k}} \rangle$$

$$\times \left(\frac{1}{\omega - \epsilon_{\mathbf{k}j} + \epsilon_{\mathbf{q}-\mathbf{k}i} + i\delta} - \frac{1}{\omega + \epsilon_{\mathbf{k}j} - \epsilon_{\mathbf{q}-\mathbf{k}i} - i\delta} \right)$$

Important technical point:

Fast integration contour for D: (Faleev)

- Tetrahedron method $\Rightarrow$ ImD on real axis.
- Hilbert transform to get ReD.

Screened Coulomb interaction: $W_{IJ}(\mathbf{q},\omega) = \left(1 - vD\right)^{-1} v$

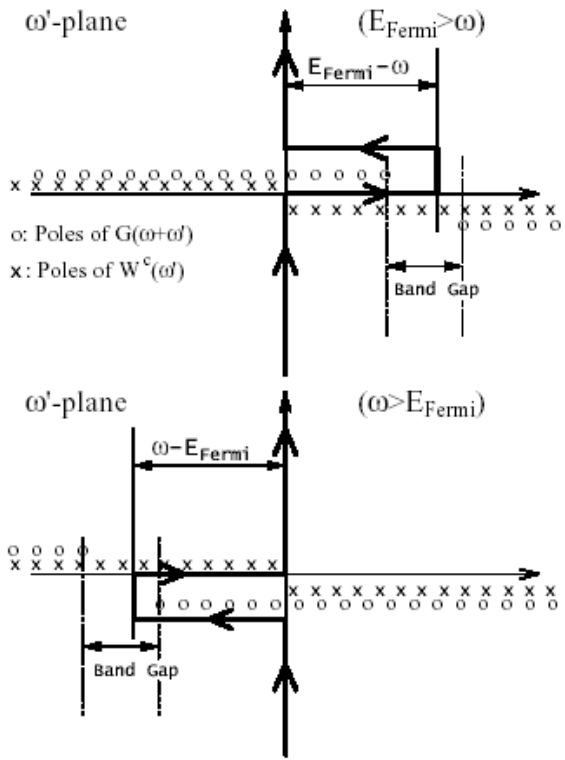
Correlation part Σ_C of self-energy

$$\langle \mathbf{q}n|\Sigma_C|\mathbf{q}n\rangle = \sum_{\mathbf{k}}^{BZ}\sum_{n'}^{\text{All}}\left\langle \psi_{\mathbf{q}n}\middle|\psi_{\mathbf{q}-\mathbf{k}n}\tilde{M}_I^{\mathbf{k}}\right\rangle\left\langle \tilde{M}_J^{\mathbf{k}}\psi_{\mathbf{q}-\mathbf{k}n'}\middle|\psi_{\mathbf{q}n}\right\rangle$$

$$\times\int_{-\infty}^{\infty}\frac{i\,d\omega'}{2\pi}W_{IJ}(\mathbf{k},\omega')\frac{1}{\omega'-\omega-\varepsilon_{\mathbf{q}-\mathbf{k}i}\pm i\delta}$$

(Use $-i\delta$ for occupied,
$+i\delta$ for unoccupied states)

Standard integration contour for Σ:



GW starting from LDA (non self-consistent)

$$\psi_{\mathbf{k}n}^{\mathrm{LDA}}(\mathbf{r}) \text{ and } \varepsilon_{\mathbf{k}n}^{\mathrm{LDA}} \rightarrow \Sigma_{\mathrm{x}}^{nn},\ D,\ W,\ \Sigma_{\mathrm{c}}^{nn}(\omega)$$

Need diagonal part Σ^{nn} of Σ at QP energies $E_{\mathbf{k}n}$.

$$E_{\mathbf{k}n} = \epsilon_{\mathbf{k}n} + \langle\Psi_{\mathbf{k}n}|\Sigma(\mathbf{r},\mathbf{r}',E_{\mathbf{k}n})|\Psi_{\mathbf{k}n}\rangle - \langle\Psi_{\mathbf{k}n}|V_{\mathrm{XC}}^{\mathrm{LDA}}(\mathbf{r})|\Psi_{\mathbf{k}n}\rangle$$

Actually make Σ at LDA $\varepsilon_{\mathbf{k}n}$. Correct by using Z factor.

$$E_{\mathbf{k}n} = \epsilon_{\mathbf{k}n} + Z_{\mathbf{k}n} \times [\langle\Psi_{\mathbf{k}n}|\Sigma(\mathbf{r},\mathbf{r}',\epsilon_{\mathbf{k}n})|\Psi_{\mathbf{k}n}\rangle - \langle\Psi_{\mathbf{k}n}|V_{\mathrm{XC}}^{\mathrm{LDA}}(\mathbf{r})|\Psi_{\mathbf{k}n}\rangle]$$

$$Z_{\mathbf{k}n} = [1 - \langle\Psi_{\mathbf{k}n}|\frac{\partial}{\partial\omega}\Sigma(\mathbf{r},\mathbf{r}',\epsilon_{\mathbf{k}n})|\Psi_{\mathbf{k}n}\rangle]^{-1}$$

Author	*Ψ-rep*	*W-rep* =	*material*	*Approx-imations*
Aryasetiawan	LAPW	LAPW	Ni	Poor basis
Aryasetiawan	LMTO (ASA)	Product basis	*d* and *f* electrons	ASA
Zein, Antropov	LMTO (ASA)	Product basis	*d* and *f* electrons	ASA, semilocal No core, self-cons
Hamada *et. al.*	LAPW	PW	Si	No core, Pl. pole
Arnaud *et al*	PAW	PW	semi-cond.	No core, ~~Pl. pole~~
Present work	smooth LMTO	PW+ PB	*d* el., semi, insulators	"self-cons"
Ku et al	LAPW	PW	Si, Ge	Self-cons

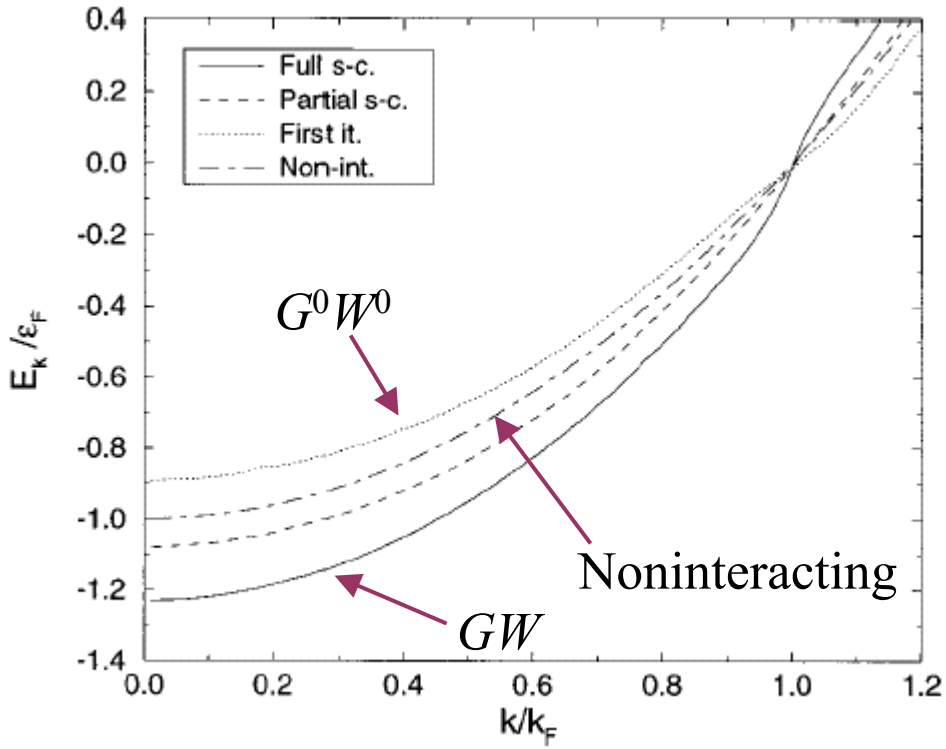
"Conventional wisdom" for QP levels from $\Sigma = G^{LDA}W^{LDA}$

(Wei Ku and A. Eguiluz, PRL **89**, 126401 (2002))

- Quasiparticle levels are accurate to ~0.1 eV
- Self-consistency "messes things up"

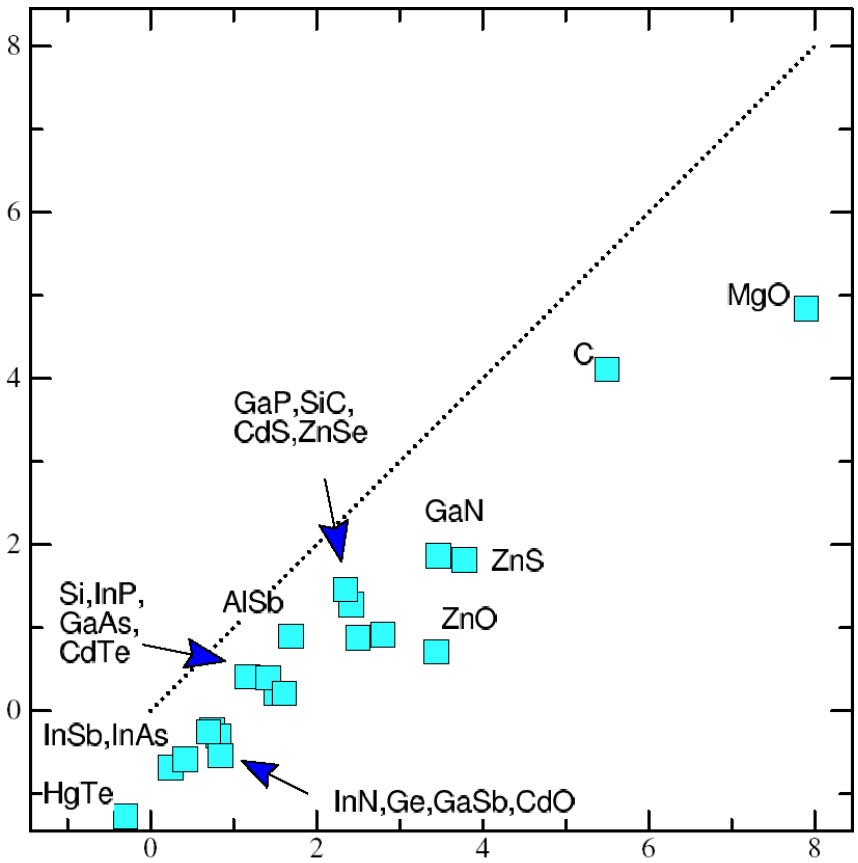
✓ Bandwidth of homogeneous electron gas widens relative to noninteracting case–when it should narrow (Holm and von Barth, PRB **57**, 2108 (1998))

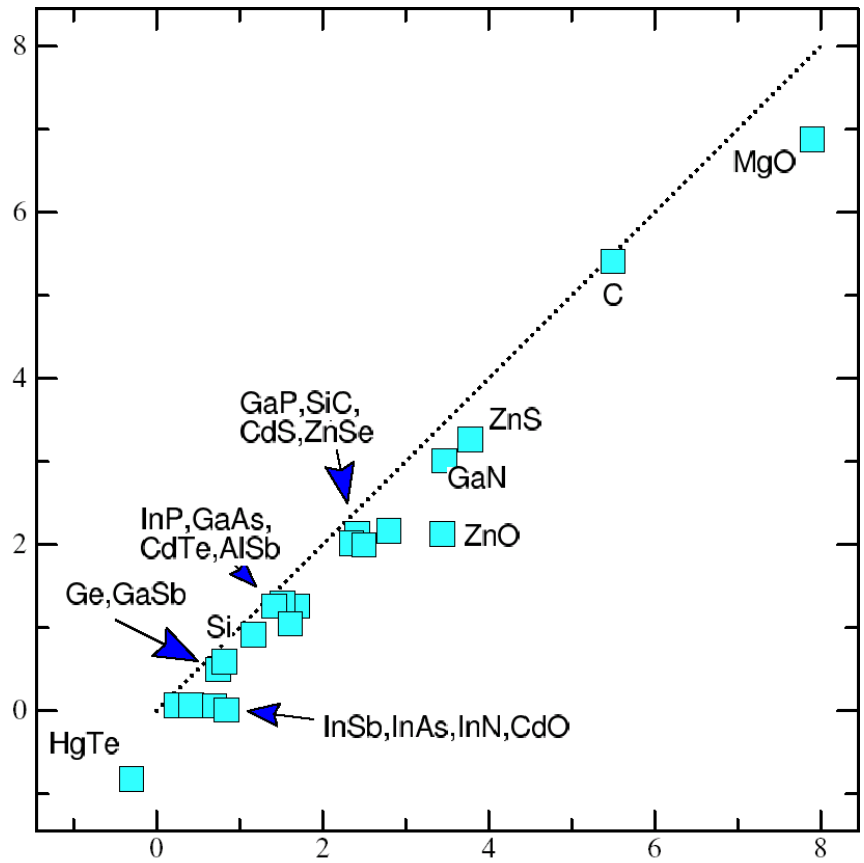
✓ Si bandgap ~1.9 eV according to PP calculation: Schone and Eguiluz, PRL 81, 1662 (1998)



- Ergo, better to stick with $G^{LDA}W^{LDA}$

Semiconductor fundamental gaps, LDA *vs* $G^{LDA}W^{LDA}$



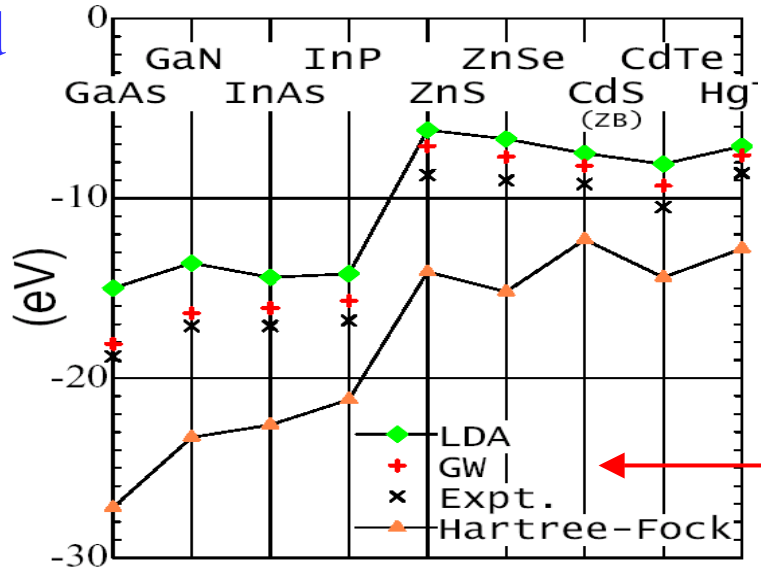


Conclusion: $G^{LDA}W^{LDA}$ is dramatically better than LDA

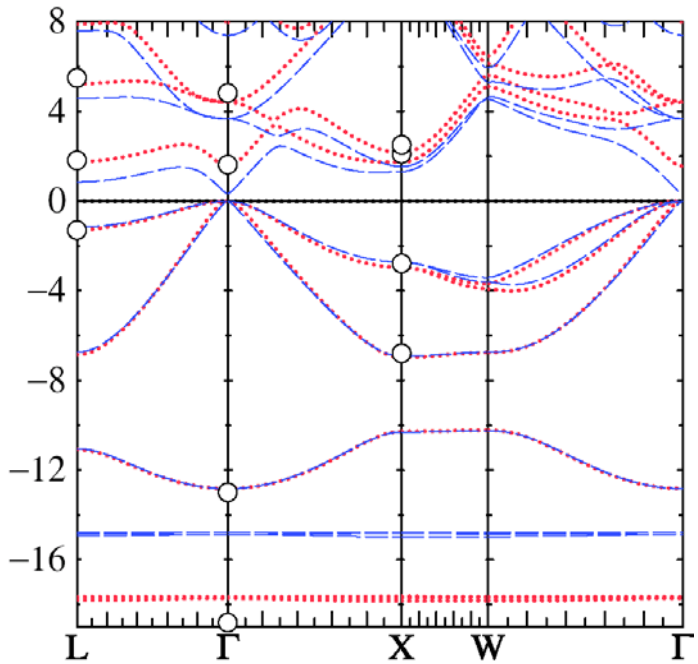
Far from 0.1 eV accuracy

Gaps systematically too small. InN gap is ~0!

Position of cation *d* levels move closer to experiment …
But shift is underestimated



$G^{\mathrm{LDA}}W^{\mathrm{LDA}}$



A slight *k*- dispersion to the gap error
(Γ–Γ error is slightly less than Γ–X error

What about self-consistency?

True RPA self-consistency: G, Σ satisfy Dyson's equation

$$G = G_0 + G_0\left(V_H + \Sigma\right)G$$

In general Σ is non-hermitian and energy-dependent.

- Norm conserving in Baym-Kadanoff sense
- An internally consistent diagrammatic treatment

Drawbacks:

- Poles of G are not on the real axis
- If $\Sigma = \Sigma(\omega)$, G partitioned into a QP part and residual satellite part.
  - The QP part has energy-dependence $Z_i/(\omega - \varepsilon_i \pm i\Gamma_i)$
  - Loss of QP weight by Z (shifted to plasmon-like satellite)
- Particle-hole pair excitations $P = -iG\times G$ reduced by factor $Z_{occ}\times Z_{unocc}$
- Result: W underscreened; also fails to satisfy f sum rule
- P and W lose physical interpretations: merely intermediate constructions during the *sc*GW cycle.
- This construction not consistent with Landau's QP theory

A self-consistency consistent with QP picture

We constrain the self-consistency as follows:

- Generate the full energy-dependent $\Sigma^{nn'}(\omega)$

n refers to basis of eigenstates of generating hamiltonian. Off-diagonal parts also calculated

- As input to the self-consistency cycle:
  - ✓Discard the non-hermitian part of Σ
  - ✓Replace by an energy-independent matrix

$$\Sigma^{nn'} = \begin{cases} \Sigma^{nn'}(\varepsilon_F) + \delta_{nn'}\left(\Sigma^{nn}(\varepsilon_n) - \Sigma^{nn}(\varepsilon_F)\right) & \text{mode 1} \\ \frac{1}{2}\left(\Sigma^{nn'}(\varepsilon_n) + \Sigma^{nn'}(\varepsilon_{n'})\right) & \text{mode 2} \end{cases}$$

A self-consistency consistent with QP picture, cont'd

$$\Sigma^{nn'} = \begin{cases} \Sigma^{nn'}(\varepsilon_F) + \delta_{nn'}\left(\Sigma^{nn}(\varepsilon_n) - \Sigma^{nn}(\varepsilon_F)\right) & \text{mode 1} \\ \frac{1}{2}\left(\Sigma^{nn'}(\varepsilon_n) + \Sigma^{nn'}(\varepsilon_{n'})\right) & \text{mode 2} \end{cases}$$

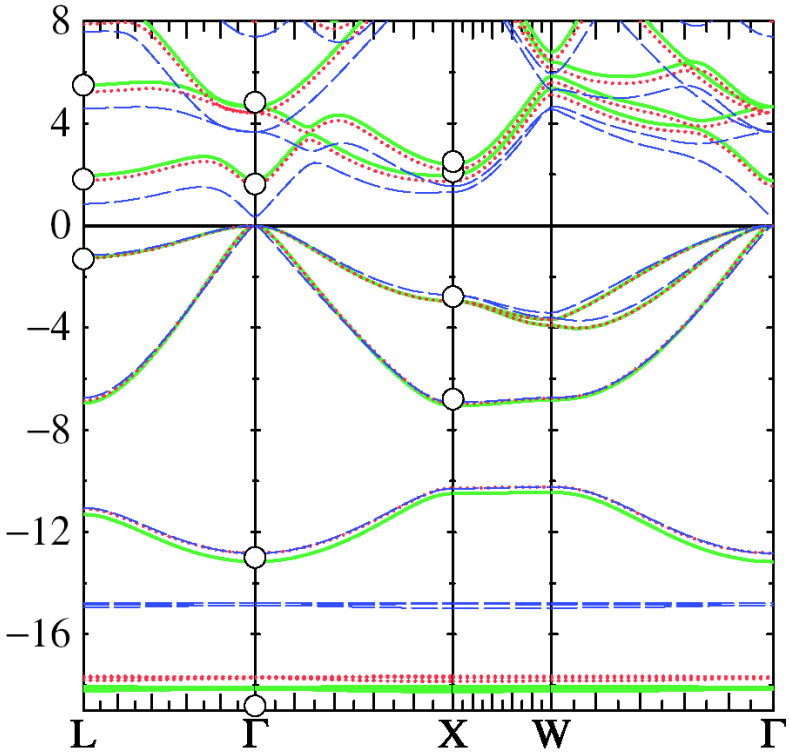
In this construction:

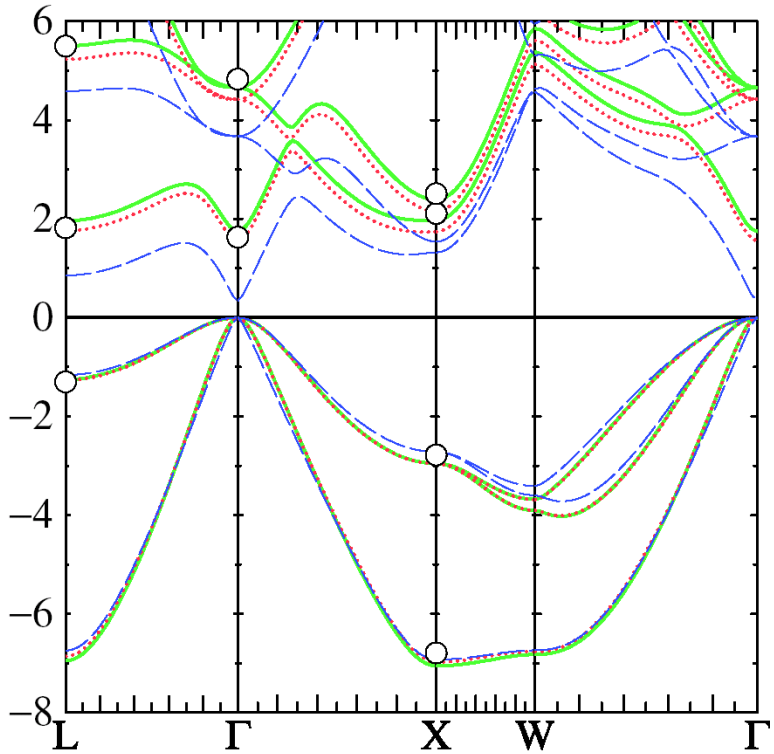
- Poles of *G* are on the real axis – compatible with QP picture
- No loss of QP weight
- Mode 1 satisfies *f* sum rule; mode 2 better at simulating true energy-dependence of Σ. Little difference in practice.
- Reasonable choice for "best possible" QP construction
- Not related to the LDA: only use LDA as a "starting guess"

Drawbacks:

- Not within the Baym-Kadanoff conserving approximation.
- Difference between present construction and the exact theory cannot be expressed as a set of diagrams.

sc*GW* results for GaAs (representative semiconductor)



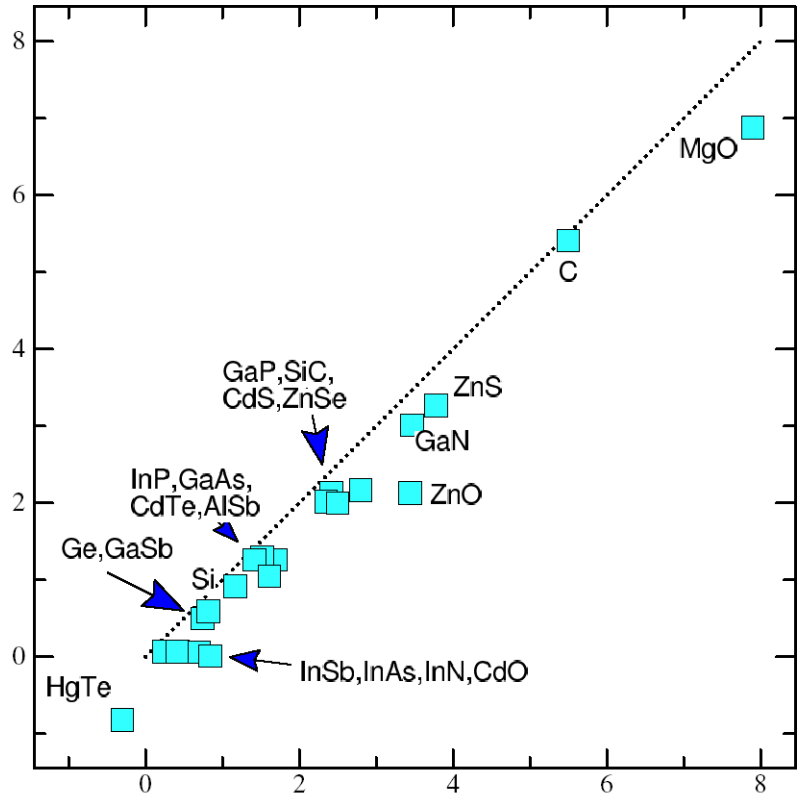


- QP levels in excellent agreement with experiment
- Slight *k* dispersion in error:

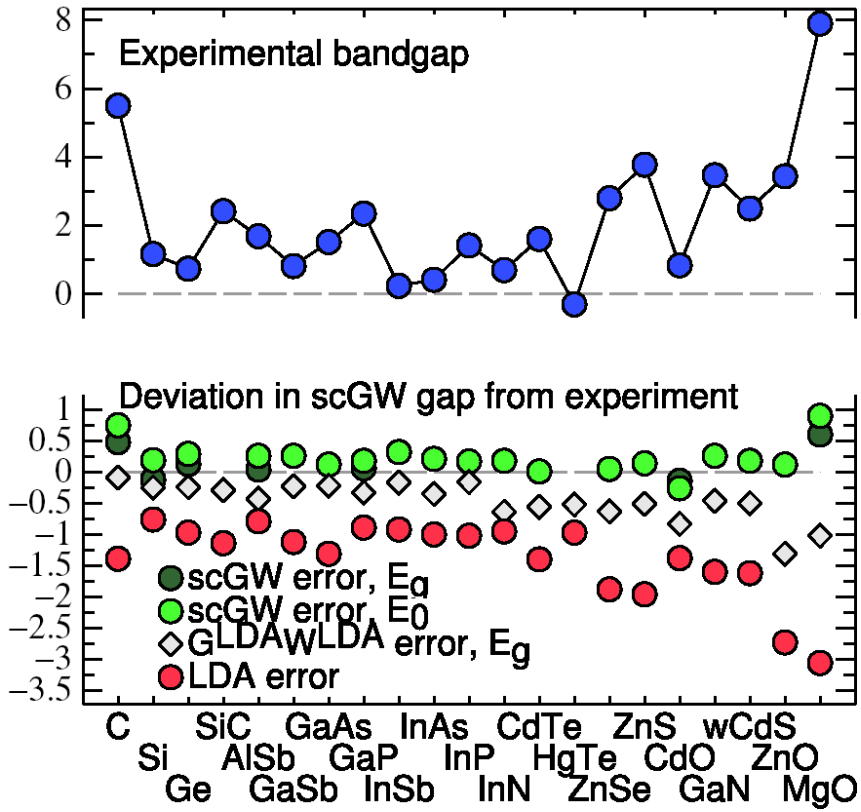
  Γ–Γ error ~0.15 eV; Γ–X and Γ–L error <0.1eV
- Ga 3*d* level shifts to near experimental value (corrects $G^{\mathrm{LDA}}W^{\mathrm{LDA}}$)
- CB effective mass = 0.074 slightly larger than experiment (0.067)

Semiconductor trends, self-consistent *GW* results

$G^{\mathrm{LDA}}W^{\mathrm{LDA}}$



GW



Near universal:

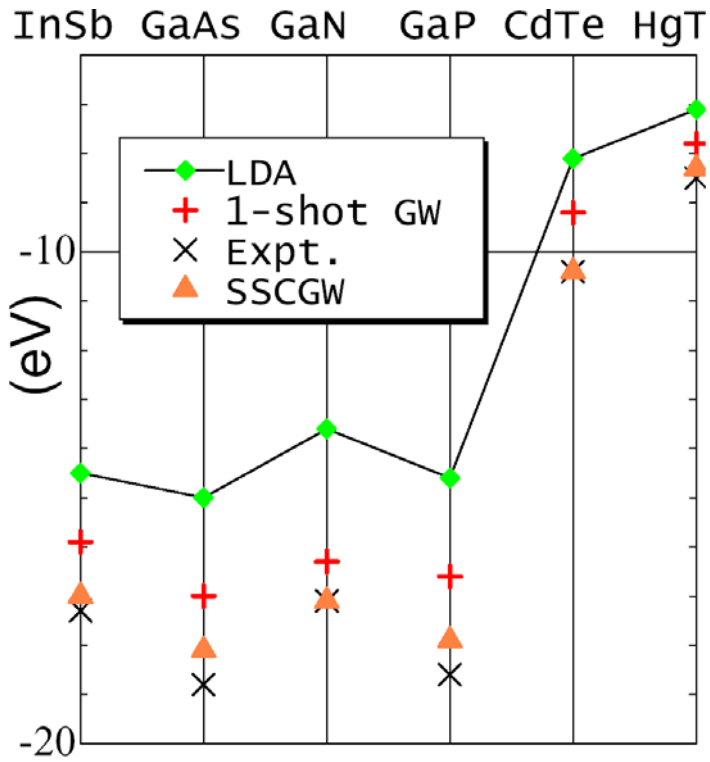
Γ–Γ slightly overestimated

Γ–X and Γ–L within ~0.1eV of experiment

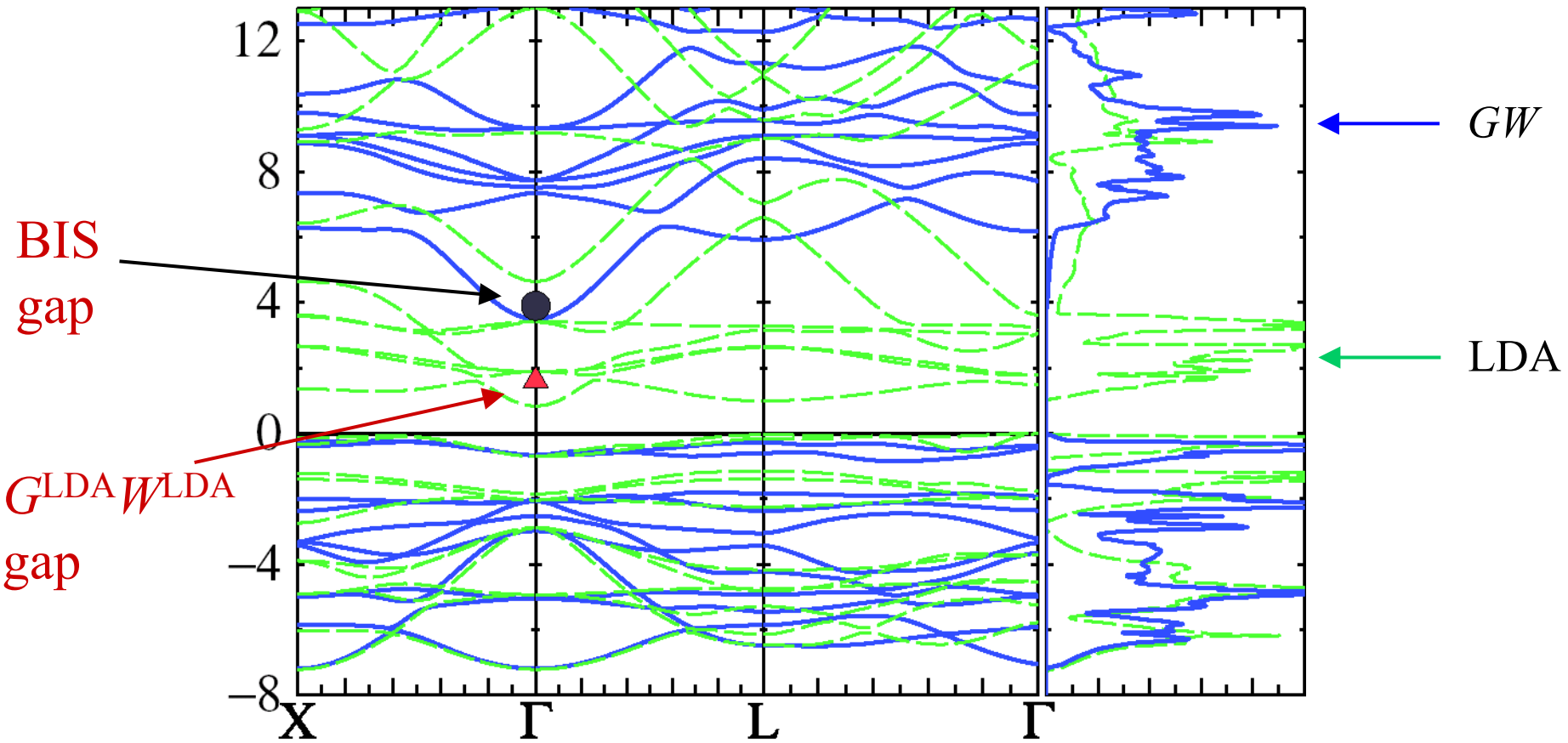
Compare to other *GW*

	PAW[3]	LAPW[4]		This work		Exp.
	$(GW)^{\mathrm{LDA}}$	$(GW)^{\mathrm{LDA}}$	scGW	$(GW)^{\mathrm{LDA}}$	scGW	
E_g	0.92	0.85	1.03	0.92	1.14	1.17
X_{1c}	1.01			1.06	1.30	1.32
L_{1c}	2.05			2.00	2.26	2.04
Γ_{15c}	3.09	3.12	3.48	3.11	3.40	3.38
Γ_{1v}		-12.1	-13.5	-12.1	-12.3	-12.5
Γ_{1v}(Ge)		-13.1	-14.8	-12.9	-13.1	-12.6

Cation core levels

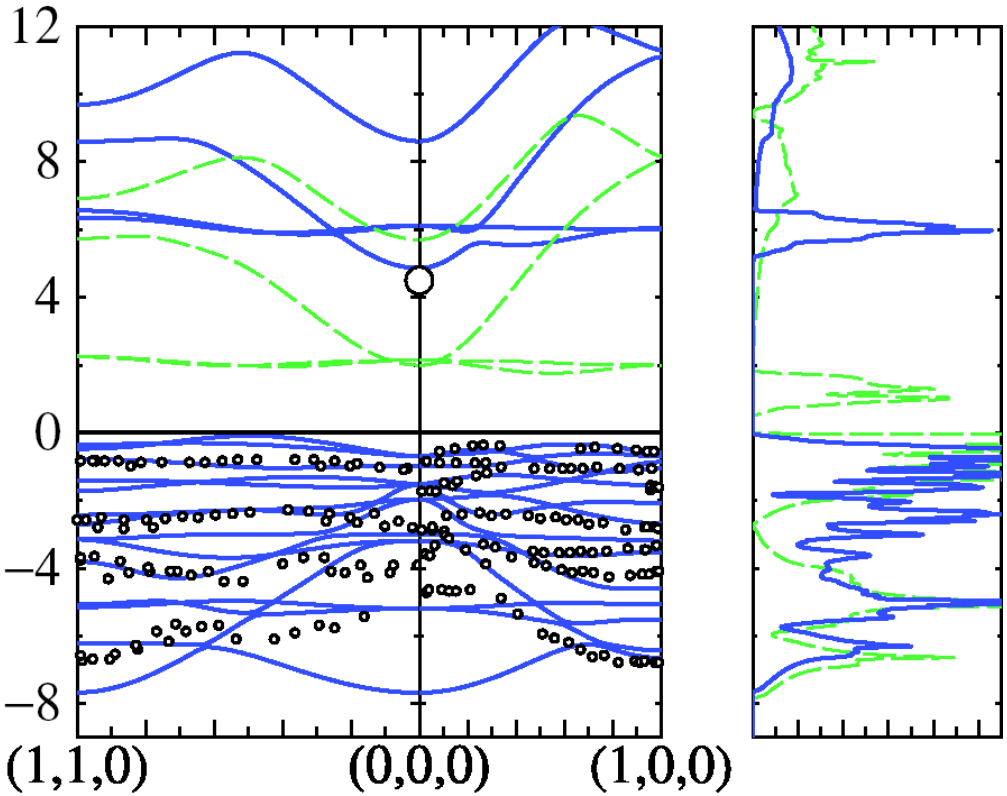


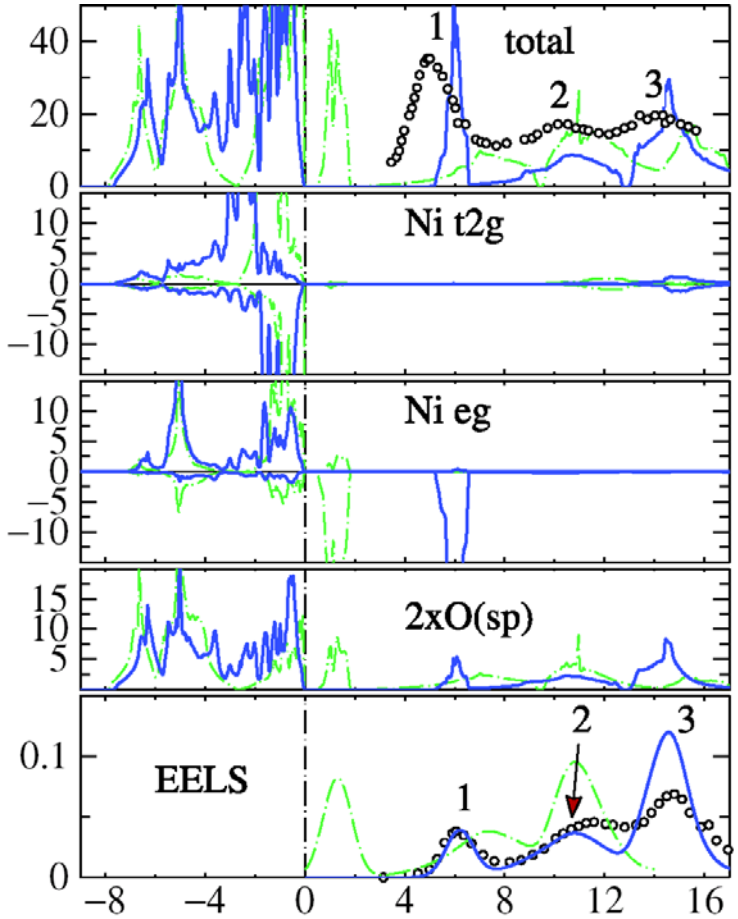
sc*GW* results for MnO



- $G^{LDA}W^{LDA}$ gap ~1.6 eV (slight improvement on LDA)
- sc*GW* gap =3.5 eV, close to experimental 3.9 ± 0.4 eV
- Conduction band dispersive *s*-like band
- Mn *d* levels shift up by ~6 eV.

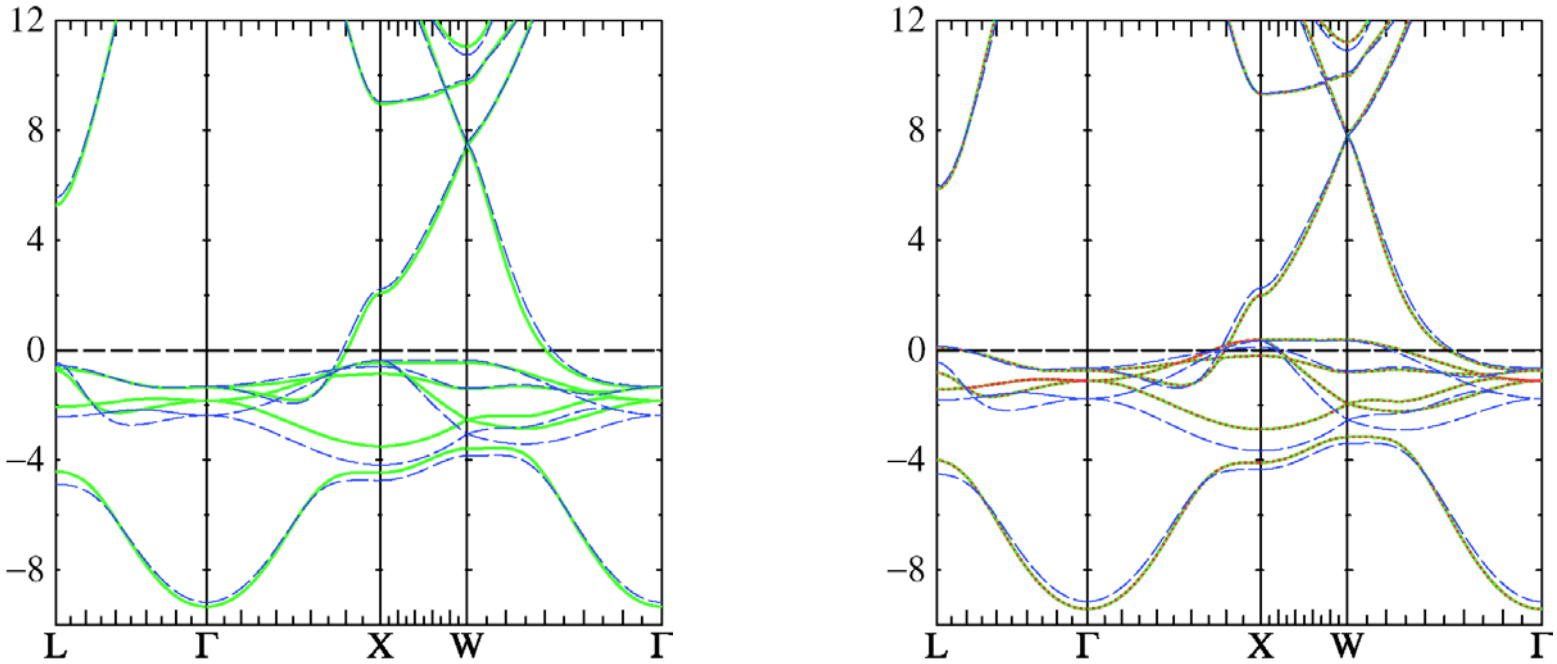
sc*GW* results for NiO





- $G^{\mathrm{LDA}}W^{\mathrm{LDA}}$: slight improvement on LDA
- sc*GW* gap =4.8 eV, slightly larger than experiment ~4.3 eV
- e_g state gets pushed down relative to LDA
- ARPES valence bands agree well with experiment
- EELS peaks, weights in excellent agreement with experiment

sc*GW* results for Ni (preliminary)

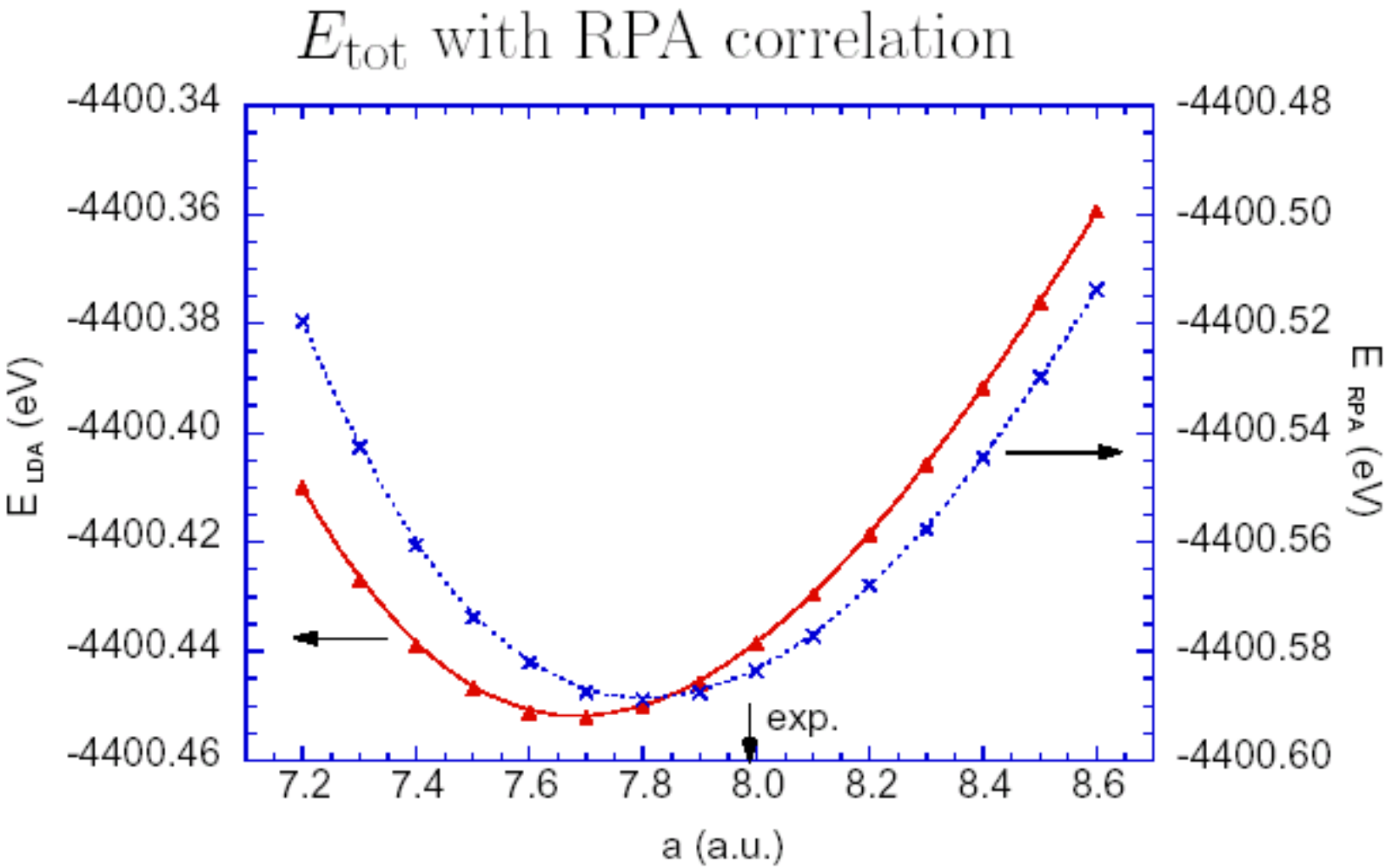


d bands narrow from 4.4 eV (LDA) to 3.9? (scGW). Expt ~3.2 eV

Magnetic moments	MnO	NiO	Ni
LDA	4.48	1.28	0.63
sc*GW*	4.76	1.72	0.74
Experiment	4.6	1.9	0.57

Volume dependence of Total energy in Na, LW functional

skip



Conclusions

- A new kind of self-consistent *GW* approximation was proposed.
- Based on results so far, this scheme has been found to be an excellent predictor of many materials properties for weakly moderately correlated materials.
- In semiconductors:
  - ✓Γ–Γ excitation systematically slightly overestimated
  - ✓A slight *k*-dependence of the gap error
  - ✓Effective masses in very good agreement with experiment
  - ✓Cation *d* levels ” ” ” ” ” ”
- scGW Ni bands narrow (not quite enough?)
- “QP” scGW does a very good job in explaining many properties of MnO and NiO
  - ✓ARPES spectra for valence band (NiO)
  - ✓BIS spectra for conduction band and bandgap
  - ✓Correct positions and weights for EELS (NiO)
  - ✓Landau QP picture not so bad for MnO, NiO after all!